



ArcheoSciences

Revue d'archéométrie

37 | 2013

Varia

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Electronic version

URL: <http://journals.openedition.org/archeosciences/3967>

DOI: 10.4000/archeosciences.3967

ISBN: 978-2-7535-2755-3

ISSN: 2104-3728

Publisher

Presses universitaires de Rennes

Printed version

Date of publication: 17 April 2013

Number of pages: 19-33

ISBN: 978-2-7535-2757-7

ISSN: 1960-1360

Electronic reference

Hussein Marey Mahmoud and Lambrini Papadopoulou, « Archaeometric Analysis of Pigments from the Tomb of Nakht-Djehuty (TT189), El-Qurna Necropolis, Upper Egypt », *ArcheoSciences* [Online], 37 | 2013, Online since 17 April 2015, connection on 01 May 2019. URL : <http://journals.openedition.org/archeosciences/3967> ; DOI : 10.4000/archeosciences.3967

Archaeometric Analysis of Pigments from the Tomb of Nakht-Djehuty (TT189), El-Qurna Necropolis, Upper Egypt

*Analyse archéométrique des pigments de la tombe de Nakht-Djehuty (TT189),
El-Qurna nécropole, la Haute-Égypte*

Hussein Marey MAHMOUD* and Lambrini PAPADOPOULOU**

Abstract: The main objective of the present work is to characterize some pigments from the tomb of Nakht-Djehuty (TT189), time of Ramesses II (c. 1279-1212 BC), El-Assasif district, El-Qurna necropolis, Luxor (ancient Thebes), Upper Egypt. The characterization of the examined wall paintings was carried out by means of optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector (EDS), X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FT-IR) and visible reflectance spectroscopy. The results revealed the characterization of the stratigraphic structure of wall decorations of the tomb and their chemical composition. The analysis of the examined samples indicated that the blue pigment was identified as Egyptian blue (Cuprorivaite), the green pigment as Egyptian green, the red pigment as red ochre, the yellow pigment as yellow ochre and the white pigment as a mixture of gypsum and calcite. The obtained results helped in identifying the chromatic palette used in one of the tombs dating back to the Ramesside period in Ancient Egypt.

Résumé: L'objectif principal du présent travail est de caractériser certains pigments de la tombe de Nakht-Djehouty (TT189), le temps de Ramsès II (c. 1279-1212 avant J.-C.), El-Assasif district, El-Qurna nécropole, Louxor (Thèbes), la Haute-Égypte. La caractérisation des peintures murales examinées a été réalisée au moyen de la microscopie optique (MO), microscopie électronique à balayage (SEM) équipé d'un détecteur d'énergie dispersive de rayons X (EDS), analyse par diffraction des rayons X (XRD), transformée de Fourier spectroscopie (FT-IR) et spectroscopie de réflectance visible. Les résultats ont révélé la caractérisation de la structure stratigraphique des décorations murales de la tombe et leur composition chimique. L'analyse des échantillons examinés ont indiqué que le pigment bleu a été identifié comme le bleu égyptien (Cuprorivaite), le pigment vert que vert égyptien, le pigment rouge comme l'ocre rouge, le pigment jaune ocre jaune et le pigment blanc comme un mélange de gypse et calcite. Les résultats obtenus a permis d'identifier la palette chromatique utilisée dans l'une des tombes datant de l'époque ramesside dans l'Égypte ancienne.

Keywords: Wall paintings, Tomb of *Nakht-Djehuty*, Ramesside period, El-Qurna, Pigments, Egyptian blue, SEM-EDS, FT-IR, XRD.

Mots-clés: peintures murales, tombeau de *Nakht-Djehouty*, période ramesside, El-Qurna, Pigments, bleu égyptien, SEM-EDS, FT-IR, XRD.

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INTRODUCTION

The Theban necropolis is one of the most popular archaeological sites in Upper Egypt. The ancient Thebes is located on the western bank of the Nile River (about 650 km south of Cairo) at the city of Luxor. The Nobles tombs at El-Qurna necropolis spread over an area of about two square miles from the necropolis of Dra Abu El-Nega in the north to Deir El Medina in the south. There are over three hundred tombs and all belong to the officials of the New Kingdom (c. 1550-1069 BC).

The Nobles tombs were funerary rooms and burial places combined (Kamil, 1976; Manniche, 1987). In ancient Egypt, color was an integral part of the substance and being of everything in life. The walls of the tombs were covered with rich and exciting catalogue of the life of man, providing some certainty of the perpetuation of life (Hodel-Hoernes, 2000). The identification of the ancient pigments and painting techniques is an indicative for the technological skills, and also for the trade trajectories. Materials analysis of artworks by modern analytical methods should be an integral part of the pre-restoration research. Generally, large number of studies has focused on the analysis and investigation of the ancient painting materials and techniques; Lucas (1962), was pioneer in the research on ancient Egyptian materials and technology, and his publication is always used as a standard reference.

In the case of wall paintings, analytical methods such as light, electron microscopy with X-ray microanalysis (SEM-EDS) and X-ray diffraction analysis are widely used. In addition, particle-induced X-ray emission (PIXE) and extended X-ray absorption fine structure analysis (EXAFS) are used successfully to identify pigments and colorants (Pagès-Camagna & Guichard, 2011). Furthermore, *in situ* analysis using portable non-invasive systems is considered a non-destructive technique and provides a rapid identification of pigments (Uda *et al.*, 2000; Uda *et al.*, 2004; Pagès-Camagna *et al.*, 2010). At present, the only alternative analytical micro method to phase analysis is vibrational spectroscopy, either Raman or IR spectroscopy. Thanks to its sensitivity to chromophores, Raman spectroscopy is particularly suitable for the identification of pigments in complex matrixes and inorganic pigments in artworks (Edwards *et al.*, 2000; Borque *et al.*, 2004; Castro *et al.*, 2005; Marano *et al.*, 2006).

The tomb of Nakht-Djehuty (TT189)

The subject of this study is the tomb of *Nakht-Djehuty* (TT189) at El-Assasif district, El-Qurna necropolis. *Nakht-*

Djehuty was the chief of carpenters and Gold workers in the Amun domain in the time of Ramesses II (c. 1279-1212 BC). The tomb entrance is located on the east wall of the court of the tomb of Kheruef. The main tomb consists of a facade, a hall, and an inner room. The outer façade of the tomb is decorated with depictions of divine barques and temple doors of gold. The hall of the tomb is decorated with scenes from the Book of Gates and scenes from a funerary procession. The inner room contains scenes of a banquet and scenes depicting *Nakht-Djehuty* kneeling before Osiris and Isis (Porter & Moss, 1994; Kitchen, 2001).

The geological structure of the necropolis

The Nobles tombs were cut in the bedrock of the Theban Mountains. The bedrock in the area is characterized with poor geotechnical properties, and therefore most of the tomb chapels were plastered and painted rather than decorated with reliefs. The Theban Mountains are consisting of about 462 meters above present sea-level; their major components are marine limestone (lower Eocene) and marls more than 350 meters thick (Said, 1962). A characteristic Esna shale formation (greenish and reddish shales with planktonic foraminifera) with thickness of about 55 meters occurs sporadically in the tombs of the area (most likely in the tombs of the Valley of Kings) (Curtis, 1979). According to Wüst & Schlüchter (2000), the rocks in the Theban Mountains consist mainly of carbonates and clay minerals with minor amounts of halite, quartz, gypsum and anhydrite. Understanding the geology of the studied area is an important aspect of characterizing the state of conservation of the tombs. It is well known that the deterioration becomes more effective in the presence of swelling clay minerals and soluble salts in the geological structure.

Research aims

The characterisation of ancient Egyptian pigments used for decorating the tombs and temples in the Theban necropolis attracted many authors (Saleh *et al.*, 1974; El Goresy *et al.*, 1986; Saleh, 1987; Uda *et al.*, 1999; El Goresy, 2000; Colinart, 2001; Lee & Quirke, 2001; Ali, 2003; Uda *et al.*, 2004; Moussa *et al.*, 2009; Marey Mahmoud, 2009; Ambers, 2010). However, the pigments used in the Ramesside tombs have not been completely examined. For this, the main research task of the present study was devoted to identify the chromatic palette used for decorating the tomb of *Nakht-Djehuty* (TT189) from the Ramesside period, El-Assasif district, El-Qurna necropolis, Upper Egypt. The analytical techniques utilized in this work were optical microscopy

(OM), scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector (EDS), X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FT-IR) and visible reflectance spectroscopy. The results of this study will help in drawing an image concerning some painting materials used in decorating one of the Nobles tombs at the Theban necropolis in Upper Egypt.

Figure 1 shows a general view of El-Assasif district, El-Qurna necropolis. The modern houses of the villages of El-Qurna at the foot of the Necropolis can be observed (fig. 1a). The tombs were cut in the bedrock of the Theban Mountains (fig. 1b). The entrance and wall decorations of the studied tomb (fig. 1c, d).



Figure 1: (a) General view of El-Assasif necropolis at western Luxor. (b) View of the Theban Mountains at El-Qurna necropolis. (c) An individual entrance of the tomb. (d) Detail of wall decorations of the tomb.

Figure 1 : (a) vue générale d'El-Assasif nécropole de l'ouest de Louxor. (b) Vue de la montagne thébaine à El-Qurna nécropole. (c) Une entrée individuelle de la tombe. (d) Détail de décorations murales de la tombe.

MATERIALS AND METHODS

Samples

Samples were carefully chosen from areas that had no aesthetic value or seriously damaged areas. Twelve tiny samples of the wall paintings including different visible colors (blue, green, red, yellow and white) were collected for analysis and to provide stratigraphic information of the paint layers. In areas show a good state of conservation,

pigment powdering is extremely limited, for this, representative very small pigment samples (a few milligrams) were carefully scraped off with a metallic scalpel.

The analytical techniques

In this work, the analytical techniques utilized to study the pigment samples were optical microscopy (OM), SEM-EDS, XRD, FT-IR and visible reflectance spectroscopy.

Optical microscopy

Tiny peaces of the painted fragments were embedded in Epoxy resin (EpoFix), cross-sectioned on variable speed silicon carbide papers and DP-lubricant blue for fine and cool polishing, and mounted on glass slides. Then, the polished cross-sections were under the reflected light using a Leitz orthoplan (binocular polarized) microscope with camera Nikon Coolpix 99.

Visible reflectance spectra

Color documentation is an integral component of any conservation project for a number of reasons; the primary purpose is to provide a stable record of the present appearance of the colors of the wall paintings at the inception of the project. Visible spectroscopy gives two types of objective measurements of colors. The first concerns the reflectance spectra which depend on the reflection of the incident light by the studied material. The reflectance spectra of pigments contain information about the dominant wavelength and the chromaticity coordinates of the analyzed material. These spectra are specific for each material, and allow approaching their nature. Also, this method measures the values of color using $L^*a^*b^*$ measurements, which is very useful for comparing different pigments and mixtures (Kartsonaki *et al.*, 2007; Vandenabeele *et al.*, 2009). The spectroscopic reflectance spectra of the different samples were obtained by a Miniscan® XE Plus spectrophotometer (HunterLab). The reflectance spectra were registered in the visible wavelengths domain (from 400 to 700 nm) over several points for each one of the different sample colors. Chromatic values are expressed as color coordinates in the CIE $L^*a^*b^*$ color system (1976) under the standard illuminant D_{65} and a 10°/observer. The spectral resolution was 10 nm, the spectral bandwidth was < 12 nm and the wavelength accuracy was 1 nm. The light source was Xenon Flash and the viewed sample area was 25 mm (1.00 in).

Sample/Oxide	Na2O	MgO	Al2O3	SiO2	SO3	K2O	CaO	FeO	CuO	SnO2	TiO2	P2O5
Preparation layer	0.79	–	1.90	7.28	68.08	–	19.41	–	–	–	0.54	–
	0.66	0.65	0.88	12.76	80.76	0.56	2.87	–	–	–	0.87	–
	0.45	–	1.21	7.76	79.54	–	10.65	–	–	–	0.43	–
Blue Pigment	3.65	1.65	2.54	49.76	7.73	0.87	12.65	0.76	17.06	0.87	–	0.83
	1.87	0.87	1.43	63.80	4.54	0.32	11.16	0.65	14.65	0.74	0.76	–
	2.85	0.97	0.86	61.36	3.76	0.94	11.82	0.86	15.33	1.1	0.65	0.60
Green pigment	3.76	1.08	1.43	62.43	4.54	0.64	15.76	0.55	6.65	0.81	–	–
	4.43	0.77	1.27	67.98	4.87	0.83	11.87	0.78	5.98	0.66	1.03	–
	2.53	0.83	0.83	71.81	3.32	0.64	14.21	0.52	4.88	0.5	1.76	0.55
Red pigment	1.03	1.78	12.04	43.24	5.76	1.34	16.91	17.80	–	–	–	0.65
	2.76	0.76	10.76	33.76	8.98	0.89	6.77	34.66	–	–	1.57	–
	1.78	0.98	16.76	43.65	2.04	1.64	6.54	26.16	–	–	1.14	–
Yellow pigment	0.85	2.06	22.91	51.08	6.65	0.77	3.16	11.17	–	–	0.87	–
	1.76	2.11	12.65	48.88	7.76	1.76	8.76	14.87	–	–	–	–
	0.97	1.43	18.76	44.32	4.43	0.45	5.76	23.65	–	–	–	–
White pigment	1.32	–	0.76	3.38	26.43	–	65.62	0.45	–	–	1.08	–
	0.85	0.44	0.67	7.65	23.65	0.44	64.76	–	–	–	–	–
	1.03	0.99	1.05	8.43	18.44	0.88	68.98	–	–	–	0.76	–

Table 1: Bulk chemical compositions (EDS analysis) of the studied samples.

Tableau 1 : Compositions chimiques en vrac (analysis EDS) des échantillons étudiés.

Scanning electron microscopy with an EDS microanalysis detector (SEM-EDS)

The microstructure and the morphological characteristics of the studied samples were performed by a JEOL JSM-840A scanning electron microscope in the backscattered electrons mode (BSE). The EDX quantitative microanalysis was carried out using an energy dispersive X-ray (EDS) Oxford ISIS 300 micro analytical system, with a detection limit of less than 1% with a confidence interval of $\pm 0.5\%$. The beam spot was 1 micrometer, the accelerating voltage 20 kV, probe current 45 nA, the working distance 20 mm and the counting time 60 s real time. The matrix correction protocol was ZAF correction.

X-ray diffraction analysis (XRD)

In order to determine the mineralogical composition of the samples, the collected samples were ground into powder in an agate mortar and were studied by X-ray powder diffraction method. X-ray diffraction measurements were carried out using a Philips PW1710 diffractometer with Ni-filtered Cu-K α radiation on randomly oriented samples. The counting statistics of the X-ray diffraction method were as follows: step size: $0.01^\circ 2\theta$, start angle: 3° , end angle: 63° , and scan speed: $0.02^\circ 2\theta/\text{sec}$. The XPOWDER analytical software was used for the semi-quantitative determination of the mineral phases. The detection limit was $\pm 2\%$ w/w.

Infrared spectroscopy

In order to collect the spectra of each color layer, a small amount of each layer was removed by micro-scalpel. Then, the sample was mixed with a freshly KBr powder (~ 150 mg). After grinding, the mixture was pressed in order to produce a pellet (with diameter of about 13 mm). The FT-IR spectra, in absorption mode, were collected using a Jasco 4100 FT-IR Spectrometer, in the spectral region 400 to 4 000 cm^{-1} at a resolution of 4 cm^{-1} . 32 scans were acquired on the samples. A database of FT-IR spectra from reference materials was used.

RESULTS

The bulk chemical composition (obtained by EDS detector) and the mineralogical composition determined by XRD method of the studied samples are given in Tables 1 and 2, respectively.

Optical examination

Figure 2 represents optical photomicrographs obtained on the examined paint layers. The microscopic examination of the blue paint layer (fig. 2a) shows the deep blue crystals of the pigment material embedded in a silica-rich matrix. The paint layer is irregular and it shows a thickness ranges

Sample/Component	C	Q	Gy	An	Cup	Pl	He	Go	Cl	Wol	Hal
Preparation layer	++	+	+++	++	—	—	—	—	—	—	+
Blue paint layer	++	+	+++	++	+	—	—	—	—	—	—
Green paint layer	++	+++	++	++	+	—	—	—	—	+	—
Red paint layer	—	+++	++	++	—	+	+	—	+	—	—
Yellow paint layer	+++	++	+++	++	+	+	—	++	+	—	—
White pigment	+++	+	+++	++	—	—	—	—	—	—	—

Table 2: The mineralogical composition of the studied samples.

Tableau 2: La composition minéralogique des échantillons étudiés

C = calcite; Q = quartz; Gy = gypsum; An = anhydrite; Cup = cuprorivaite; Pl = plagioclase; He = hematite; Go = goethite; Cl = clay minerals (kaolinite type), Wol = wollastonite; Hal = halite.

— = not determined; + = traces; ++ = minor constituent; +++ = major constituent.

Légende en français ?

from is 50-90 μm . Also, greenish-blue hues were observed in different areas on the sample. The optical examination of the green paint layer (fig. 2b) shows the slightly thick pigment layer (70-100 μm) with greenish-turquoise color. The optical examination of the red pictorial layer (fig. 2c) shows a brilliant irregular layer with thickness ranges from 50-80 μm . In case of the yellow pictorial layer, the optical examination shows the irregular yellow pigment layer with thickness ranges from 50-70 μm (fig. 2d). Different particles with red and brown hues are clearly noticed beneath the paint layer.

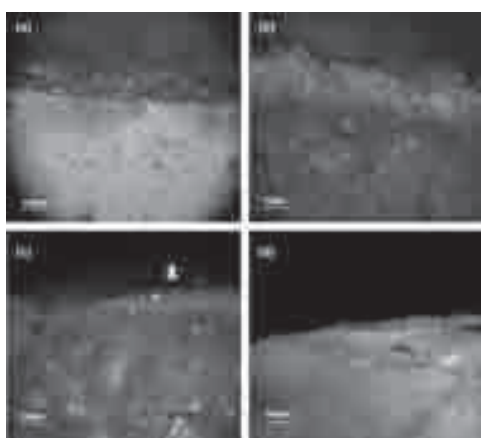


Figure 2: (See colour plate) Optical photomicrographs obtained on polished cross-sections of the paint layer.

Figure 2: (Voir planche couleur) Microphotographies optiques obtenues sur polies des sections transversales de la couche de peinture.

- (a) The blue paint layer. (b) The green paint layer. (c) The red paint layer. (d) The yellow paint layer.
(a) la couche de peinture bleue. (b) La couche de peinture verte. (c) la couche de peinture rouge. (d) La couche de peinture jaune.

Visible reflectance spectra

Figure 3 displays the reflectance spectra registered on the pigment samples and Table 3 summarizes the $L^*a^*b^*$ co-ordinates of the studied samples. The reflectance spectra of the Egyptian blue pigment samples (fig. 3a) show a slope at the wavelength higher than 650 nm. The green pigments tend to give a sharp slope at wavelength higher than 630 nm and return to increase after this wavelength (fig. 3b). The samples show different dominant wavelengths in the greenish-yellow zone meanly at 570 nm. Some chromatic changes of the blue pigment mainly in form of green colors

Chromatic coordinate CIE (1974) color system			
Color	L^*	a^*	b^*
blue pigment	72.43	-4.54	-7.65
	68.87	-6.89	-9.54
	66.54	-7.75	-5.65
	66.43	-5.48	-8.76
	62.43	-6.42	-7.33
	71.43	-4.33	-5.43
	63.54	-5.21	-5.22
	64.03	-3.54	-9.54
green pigment	65.88	-9.78	4.54
	66.54	-8.68	5.43
	65.89	-11.32	6.54
	66.54	-7.54	4.66
	66.32	-7.66	4.98
	65.23	-8.88	5.43
	69.55	-12.43	7.65
	68.32	-6.77	7.43
yellow pigment	71.83	9.09	14.77
	70.34	9.21	15.39
	69.65	7.51	19.57
	70.54	7.65	19.35
	70.43	7.83	20.43
	68.54	8.65	20.87
	69.55	9.76	21.43
	69.08	8.32	17.65
red pigment	49.65	5.52	21.34
	50.43	25.55	20.42
	55.87	9.87	18.76
	56.76	9.76	19.65
	49.65	7.65	19.65
	52.54	9.87	20.65
	59.87	9.54	20.09

Table 3: The chromatic coordinates $L^*a^*b^*$ (CIE 1976 color system) measured for the pigment samples.

Tableau 3: Les coordonnées chromatiques $L^*a^*b^*$ (système de couleurs CIE 1976) mesurées pour les échantillons de pigments.

are chromatically characterized by a small shift at 520 and 580 nm. The reflectance spectra of hematite (fig. 3c) show a sharp positive slope at wavelengths higher than 600 nm, while goethite show a slope lower than 600 nm (fig. 3d). According to Gil *et al.* (2009), hematite can be characterized by the presence of a sharp positive slope at wavelengths higher than 560 nm. For pure goethite, the first slope is observable at around 450 nm, followed by a sharp peak

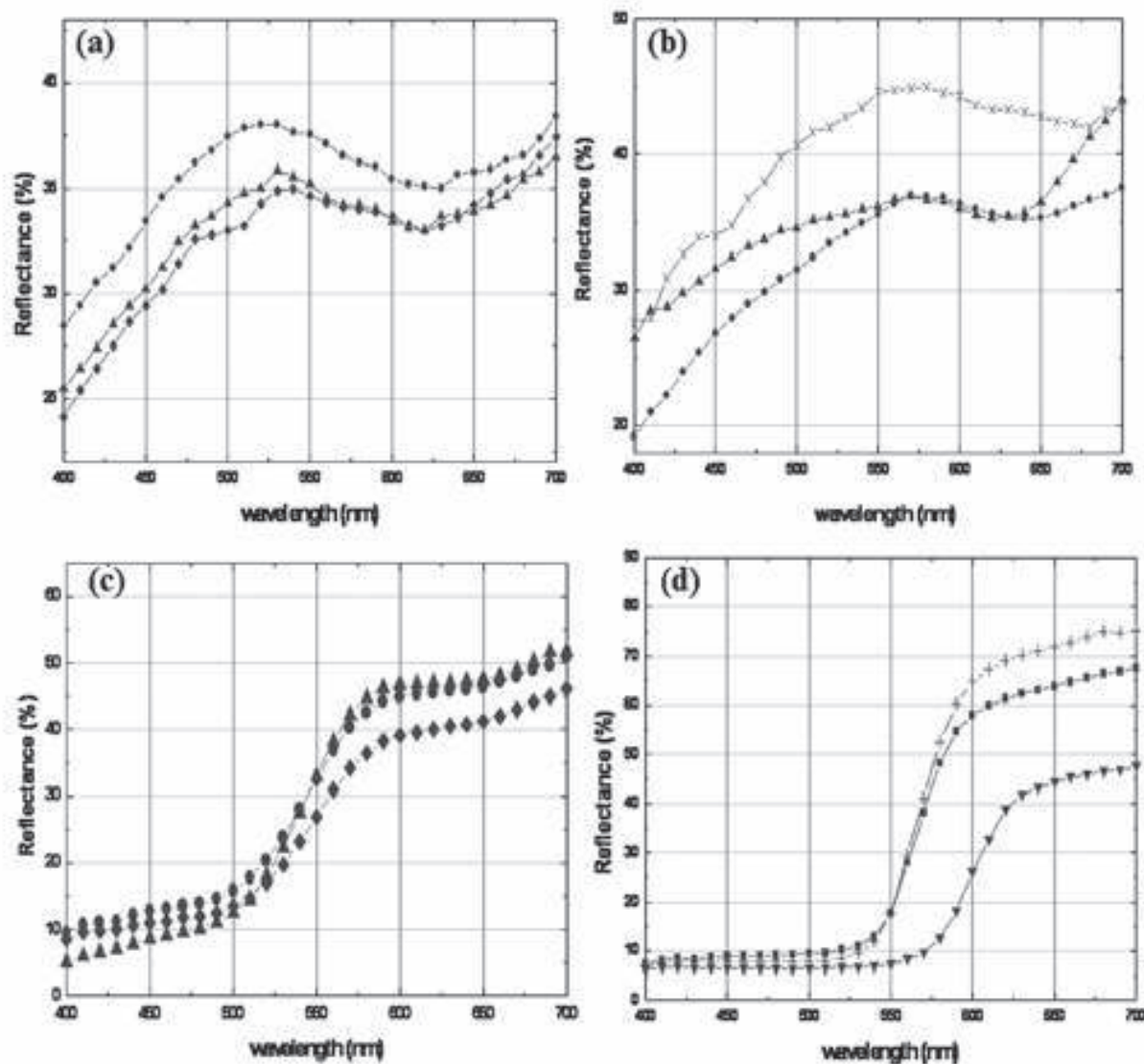


Figure 3: The reflectance spectra (%) recorded on the pigment sample.

Figure 3: Les spectres de réflectance (%) enregistré sur l'échantillon de pigment.

(a) The blue pigment. (b) The green pigment. (c) The yellow pigment. (d) The red pigment.

(a) le pigment bleu. (b) Le pigment vert. (c) le pigment jaune. (d) le pigment rouge.

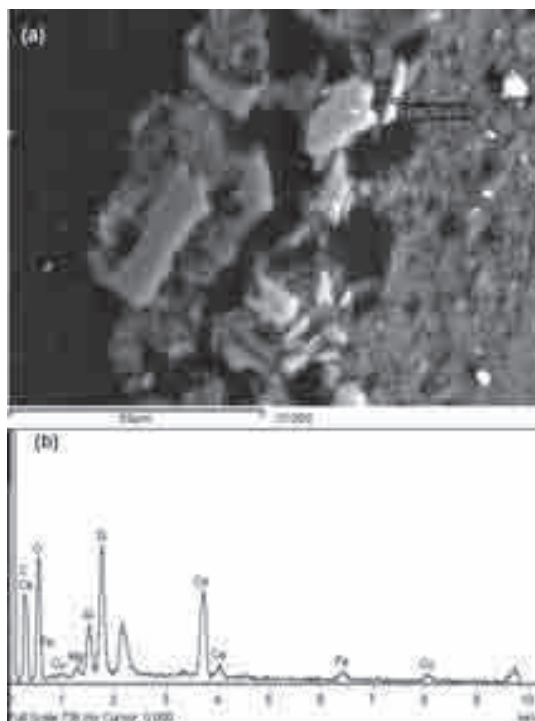


Figure 4: (a) BSE image obtained on a cross-section of the blue paint layer. (b) An EDS spectrum obtained on the same sample.

Figure 4: (a) L'image obtenue sur l'BSE une section transversale de la couche de peinture bleue. (b) Un spectre EDS obtenu sur le même échantillon.

at around 500 nm. The yellow paint layers showed high L^* value (stands between 68.54 and 71.83) representing a slightly brilliant appearance compared to the red ones. The yellow ochre (mainly of goethite) are characterized by a small value of a^* (smaller than 10), whereas the red ochre (mainly of hematite) show a high value of a^* (larger than 25).

The analysis carried out on the green surfaces showed negative a^* values (stands between -12.43 and -6.77) indicating green color, with only positive b^* values (for yellow). The blue paint layers denoted negative b^* values (stands between -9.54 and -5.22, correspond to blue), together with negative a^* values which indicate green hues. The $L^*a^*b^*$ values enabled color comparison in terms of the brilliance and tone of the pigmented surfaces. The reflectance spectra helped to identify and differentiate the different colors of the samples and in particular the red and yellow ochre, as well as between Egyptian blue and Egyptian green. The composition of pigments can be identified depending on the shapes and the peak positions of their reflectance spectrum curves (Torrent & Barrón, 2002; Wang *et al.*, 2005). The shade of

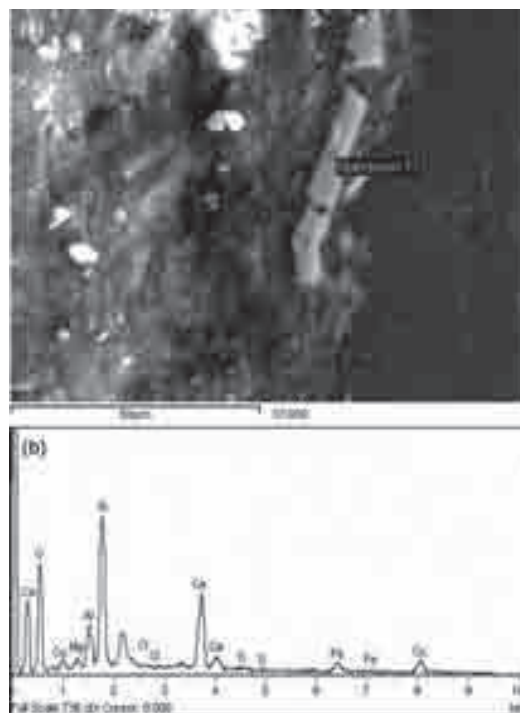


Figure 5: (a) BSE image obtained on a cross-section of the green paint layer. (b) An EDS spectrum obtained on the same sample.

Figure 5: (a) L'image obtenue sur l'BSE une section transversale de la couche de peinture verte. (b) Un spectre EDS obtenu sur le même échantillon.

the Egyptian blue is strongly related to the coarseness and fineness of the pigment as it was determined by the degree of aggregation of the Egyptian blue crystals. Aging of the pigments is reflected by the blunting of characteristic peaks and for ochre by a general transposition of the plot attributed to the loss of luminosity (Kartsonaki *et al.*, 2007). The chromatic differences between surfaces of similar shades can be ascribed to the natural impurities associated to the pigment and also to the different concentrations of the pigment in the medium (the underlying gypsum layer).

Microstructures and microanalysis

The polished cross-sections of the paint layers were investigated by the scanning electron microscopy using the backscatter detector mode (BSE). The backscattered electrons image (BSE) obtained on a polished cross-section prepared on the blue paint layer (fig. 4a) shows the coarse skeletal crystals (typically < 100-150 μm in length). Also, angular large particles of quartz and aggregates of the underlying

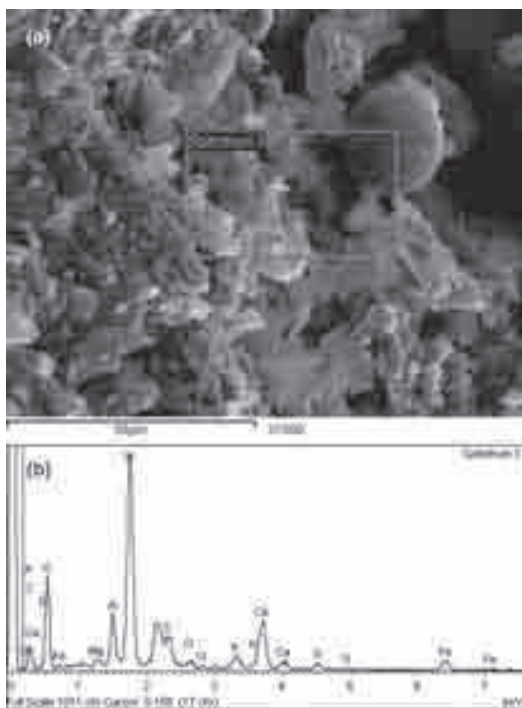


Figure 6: (a) SEM image obtained on the outer surface of the red paint layer. (b) An EDS spectrum obtained on the same sample.

Figure 6 : (a) L'image SEM obtenu sur la surface extérieure de la couche de peinture rouge. (b) Un spectre EDS obtenu sur le même échantillon.

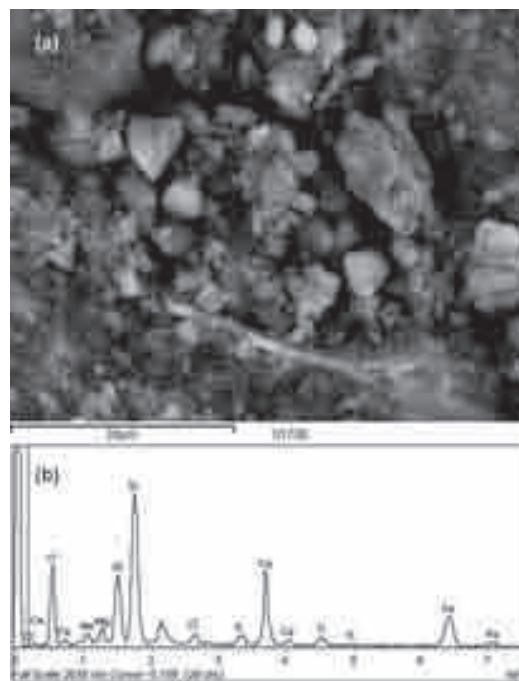


Figure 7: (a) BSE image obtained on the outer surface of the yellow paint layer. (b) An EDS spectrum obtained on the same sample.

Figure 7 : (a) L'image BSE obtenu sur la surface extérieure de la couche de peinture jaune. (b) Un spectre EDS obtenu sur le même échantillon.

ground layer can be observed. Moreover, we can see that the silica-rich matrix in the sample partially has been lost from the Egyptian blue probably due to the weathering processes. By the optical examination of the sample (see fig. 2a), many voids and free spaces were observed and the color was pale blue and that is probably due to the dissolution of glass phases and the original pigment layer mainly be the effect of salt weathering. The EDS spectrum obtained on the same sample (fig. 4b) shows major elements of silicon, sulfur and calcium. Minor elements of aluminum, sodium, magnesium, copper, chlorine, potassium and iron were also measured. Silicon (31.89%), calcium (12.61%) and copper (6.78%) were detected which form the chemical formula of cuprorivaite ($\text{CuCaSi}_4\text{O}_{10}$). The high silica content (49-63%) together with the bulk alumina (0.86-2.54%) and iron oxide (0.65-0.86%) contents suggest that sand provided the source of the quartz. The alumina content of the pigment is probably associated with feldspar impurities present in the sand (Pagès-Camagna & Colinart, 2003). The continuous analysis on several points on the blue pigment

samples shows the detection of variable amounts of tin oxide (SnO_2) greater than 0.86%. This suggests that a scrap of bronze was used as a source for copper in producing the pigment. Jaksch *et al.* (1983) and El Goresy (2000) had previously reported that till the reign of Tuthmosis III (the 18th Dynasty, c. 1490-1436 BC), probably bronze filings were applied as a starting material in producing the Egyptian blue and green frits. Their results were built up on the basis of the frequent presence of tin rich phases (*i.e.* cassiterite (SnO_2) and malayaite (CaSnSiO_5) in the examined samples. The detection of sodium, potassium and magnesium together are all most probably associated with the alkali flux used in producing the pigment. The possible sources of the soda-rich alkali are the natural evaporite, natron (Tite, 1987), and soda-rich plant ashes (Jaksch *et al.*, 1983) obtained from burning coastal and desert plants.

The BSE image obtained on an individual grain in the turquoise-green paint layer (fig. 5a) shows slightly large copper calcium-silicate crystals embedded and scattered on the preparation layer. An EDS spectrum obtained on the

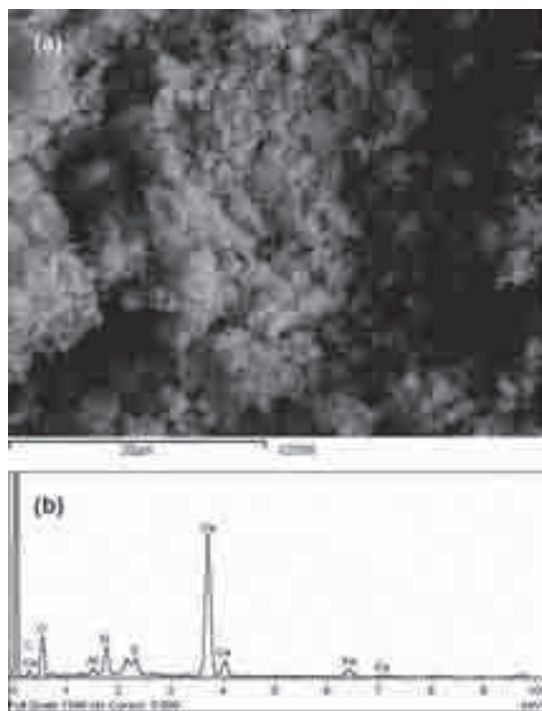


Figure 8: (a) SEM image obtained on the white paint layer. (b) An EDS spectrum obtained on the same sample.

Figure 8: (a) L'image SEM obtenu sur la couche de peinture blanche. (b) Un spectre EDS obtenu sur le même échantillon.

sample (fig. 5b) shows the high ratio of silicon in the sample, while calcium and copper were also detected with other elements of magnesium and chlorine. The microanalysis of several points on the green pigment samples shows high contents of silica (62-71%, SiO_2) and soda (2.53-4.43%, Na_2O) together with variable amounts of tin oxide (0.5-0.8%, SnO_2). The SEM image obtained on the red pictorial layer (fig. 6a) shows coarse aggregates of the pigment material and large grains of quartz are also notable. An EDS spectrum obtained on the sample (fig. 6b) shows the peak of iron (3-17%) is present, which indicates the existence of an iron oxide. The strong contribution of aluminum (11-27%) and silicon (21-44%) detected in the sample indicates a possible existence of an aluminosilicate material (Zorba *et al.*, 2007). The detection of sulfur and calcium in the sample suggests the existence of calcium sulfates probably come from the underlying preparation layer. Other elements of magnesium, chlorine and titanium were also measured. The BSE micrograph obtained on the yellow pigment sample (fig. 7a) shows the fine-grained crystals of the

pigment material with large grains of calcium sulfate phases. The microanalysis of the sample (fig. 7b) shows the presence of iron (4-8%) indicating possible existence of an iron oxide. The detection of aluminum (9-33%) and silicon (28-47%) indicates the existence of an aluminosilicate material (probably clay minerals). The BSE micrograph obtained on the white pigment sample (fig. 8a) shows fine small grains of calcite and slightly large ones of gypsum. The microanalysis of the sample (fig. 8b) shows major signals of calcium together with small contribution of sulfur, silicon, aluminum and iron.

Mineralogical characterization (XRD)

Representatives XRD patterns of the paint layers are given in Figure 9. XRD measurements performed on the preparation layer showed that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the predominant phase in the sample. Minor amounts of anhydrite (CaSO_4) and calcite (CaCO_3) were also determined. Traces of quartz (SiO_2) and sodium chloride (halite, NaCl) were also measured. XRD analysis of the blue paint layer (fig. 9a) shows that the main constituent is gypsum with minor amounts of anhydrite and calcite. Traces of quartz and cuprorivaite were also determined. XRD analysis of the green pigment sample shows that quartz is the major component, with minor amounts of anhydrite, gypsum and calcite. Traces of wollastonite (CaSiO_3) and cuprorivaite were also measured. XRD analysis of the red pigment sample showed that quartz is the main component; with minor amounts of gypsum, anhydrite and calcite. Traces of hematite ($\alpha\text{-Fe}_2\text{O}_3$), plagioclase ($\text{NaAlSi}_3\text{O}_8$) and clay minerals (kaolinite type) were also determined. XRD analysis of the yellow pigment sample showed that the sample consists mainly of gypsum, with minor amounts of anhydrite and goethite ($\alpha\text{-FeOOH}$). Traces of plagioclase and clay minerals were also measured. XRD analysis of the white pigment (fig. 9b) show that the sample consists mainly of gypsum and calcite. Minor amounts of anhydrite and traces of quartz were also measured.

FT-IR results

An absorbance FT-IR spectrum recorded on a dark blue pigment is shown in Figure 10. The spectrum shows that the Egyptian blue pigment represents characteristic peaks in the region 1280 and 1000 cm^{-1} are attributed to Si-O-Si stretching vibrations. Egyptian blue shows a typical triplet at 1006, 1057 and 1162 cm^{-1} and a shoulder at about 1250 cm^{-1} (Mazzocchin *et al.*, 2004). The FT-IR spectrum recorded on a white paint layer shows the

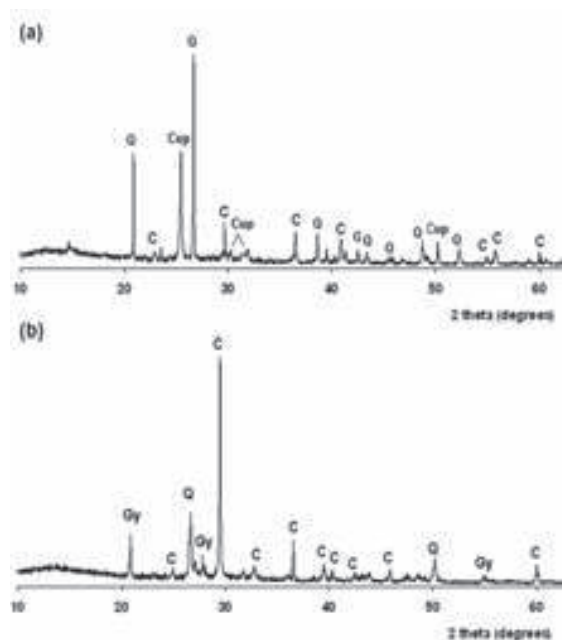


Figure 9: Representatives XRD patterns of paint layers.
 Figure 9: Représentants motifs XRD de certaines couches de peinture.
 (a) Blue paint layer. (b) White paint layer.
 (a) une couche de peinture bleue. (b) couche de peinture blanche.

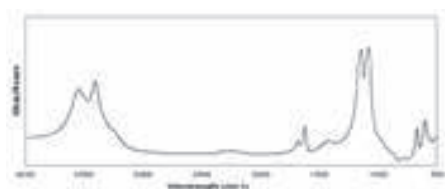


Figure 10: An absorbance FT-IR (KBr) spectrum collected on a deep blue pigment.
 Figure 10 : Une absorbance de FT-IR (KBr) spectre collectées sur un pigment bleu.

characteristic bands of calcite at 1437, 715 and 876 cm^{-1} are present. Moreover, the contribution of the gypsum band at 1 172 cm^{-1} is probably corroborated for the appearance of the band at 3 450 cm^{-1} . FT-IR spectra obtained on the red pigment present peaks at 465 and 550 cm^{-1} are attributed to the presence of iron oxide, while the shoulder at 1 161 cm^{-1} , the double peak at 796 and 776 cm^{-1} and the single peaks at 690 are indicative for the presence of red ochre and quartz

(Bikiaris *et al.*, 1999; Hein *et al.*, 2009). FT-IR spectra collected on the yellow pigment sample shows the bands at 797 and 902 cm^{-1} are assigned to the vibrational modes of goethite (Franquelo *et al.*, 2009). The bands at ~3620 and 3 696 cm^{-1} is due to free hydroxyl ions of kaolinite (a clay mineral is usually associated to ochre pigments), peaks of water H-O-H str., and a broad peak at 3 140 cm^{-1} which was attributed to the peak of hydrated ferric oxide.

DISCUSSION

Blue pigment

Egyptian blue was identified as the blue coloring materials used in the tomb. The EDS microanalysis showed the detection of tin in the samples suggesting that a scrape of bronze rather than copper ore was as the starting material for producing the pigment. In their study of pigments from the temple of Seti I in Abydos (Egypt) (19th dynasty, c. 1293-1185 BC), Pavlidou *et al.* (2008) reported that the pigments used in decoration of the temple were identified as Egyptian blue, Egyptian green, red and yellow ochre and paint layers were applied in thin layers, as it was common in this period of time.

Green pigment

The green pigment was characterized as Egyptian green; and as in the case of the Egyptian blue samples, an alloy of bronze was used for producing the pigment. According to Uda (2004), the green colored parts in the walls of the tomb of Amenhotep III at the Theban necropolis were found to contain Egyptian blue and goethite.

Yellow pigment

The yellow pigment was identified as yellow ochre (goethite mixed with clays and silicates). FT-IR and XRD data revealed the presence of goethite, and the EDS microanalysis showed that the peak of iron is present. The hue of goethite is affected by its crystallinity and elemental purity. Finely particulate (poorly crystalline) goethite, commonly called limonite in the past, is brownish yellow. Goethite only uniquely occurs in nature in a pure form or as a massive mineral (Ortega *et al.*, 2001; Ruan *et al.*, 2002; Hradil *et al.*, 2003). In wall paintings dating back to the Ramesside time at the necropolis of Saqqara, Marey Mahmoud *et al.* (2011) reported that the yellow pigment used in the decoration

of the tomb of *hwi nfr* was identified as a blended layer of yellow ochre and orpiment (As_2S_3).

Red pigment

The red color was obtained by using red ochre. The EDS analysis showed the extensive existence of iron in great proportions in the studied samples. A small contribution of silicon and aluminium may indicate the presence of aluminosilicate materials (*e.g.* clays). Clays generally of the kaolin group and quartz are by far the most commonly found accessory minerals in the red/yellow earths and are also often found in earth pigments (Zorba *et al.*, 2007).

White pigment

From the XRD and FT-IR analyses, the white pigment was identified as a mixture of calcite and gypsum. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) occur together in many Miocene formations in Egypt. There is no exact time of the first application of gypsum or anhydrite in decoration in ancient Egypt, and it may be used from the 5th Dynasty till the Roman time (El Goresy *et al.*, 1986). Lee and Quirke (2001) reported that the analysis of a white pigment from Theban tombs dated back to the 12th Dynasty, the 18th Dynasty, and from the 20th Dynasty (*c.* 1185-1070 BC) revealed magnesian calcite, chosen for its intensity as a first layer under the main pigment.

CONCLUSIONS

The application of different analytical techniques such as optical microscopy, SEM-EDS, XRD, FT-IR and visible reflectance spectroscopy was really helpful to identify the chromatic palette used in the tomb of *Nakht-Djehuty* (TT189), El-Assasif district, El-Qurna necropolis, Upper Egypt. The analyses used in this work provide useful information about the stratigraphy of the paint layers and their chemical composition in addition to their chromatic characteristics. The optical examination of the paint layers showed that pigments were applied in form of thin layers on a preparation layer of gypsum. The identification of the studied pigments showed that the blue pigment was identified as Egyptian blue (cuprorivaite, $\text{CaCuSi}_4\text{O}_{10}$), the green pigment as Egyptian green (Cu-wollastonite, $[(\text{Ca,Cu})_3(\text{Si}_3\text{O}_9)]$), the red pigment as red ochre (hematite, $\alpha\text{-Fe}_2\text{O}_3$), the yellow pigment as yellow ochre (goethite, $\alpha\text{-FeOOH}$) and the white pigment as a mixture of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcite (CaCO_3).

The EDS microanalysis of the Egyptian blue and green pigment samples revealed the detection of variable amounts of tin oxide (SnO_2) in the samples. These findings suggest that a scrape of bronze rather than copper ores was used to produce the pigments. The visible reflectance spectra recorded on the samples allowed the identification of the different pigments and to distinguish their chromatic hues. These reflectance spectra will be used as reference for long-term monitoring of the state of conservation of the wall paintings in the tomb. In conclusion, further investigation of additional pigment samples will be of importance to increase our knowledge of the materials used during this period of the Egyptian history.

Acknowledgements

The author is grateful to Mr G. Mechalidis and Mr V. Kyriakopoulos, Department of Mineralogy-Petrology-Economic Geology, School of Geology of Aristotle University of Thessaloniki, Greece for their help through the optical examination of the cross-sections.

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